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(54) **SURFACES IMPERMEABILISEES STRUCTUREES
COMPRENANT DES ZONES CONTENANT UN POINT
PARTICULIER DE MOUILLAGE**

(54) **STRUCTURED LIQUID-REPELLENT SURFACES HAVING
REGIONS WHICH ARE LIQUID-WETTING IN A DEFINED
LOCATION**

(57) The present invention relates to structured surfaces having protuberances having a mean height of 50 nm to 10 μ m and a mean spacing of 50 nm to μ m, a surface energy of the unstructured material of less than 35 mN/m and liquid-wetting regions and processes for the production of such surfaces. Structured surfaces according to the invention can be used for the production of sample carriers for instrumental analysis, of sample carriers with liquid-conducting systems (microfluidics), as a structured reaction site for reagents and analytes for diagnostic systems (Lab on Chip) or for the production of nanotiter or microtiter sample carriers.



STRUCTURED LIQUID-REPELLENT SURFACES HAVING
REGIONS WHICH ARE LIQUID-WETTING IN A DEFINED LOCATION

5 The present invention relates to articles having structured surfaces which are made of a material having a medium to low surface energy and which have regions that are liquid-wetting.

The present invention furthermore relates to processes for the production of these articles and their use.

10 Articles having poorly wettable surfaces possess a number of interesting and economically important features. Thus, they are easy to clean and do not readily retain residues and liquids.

Surfaces from which liquids, such as water, readily run off must be either very hydrophilic or hydrophobic.

15 Hydrophilic surfaces have small contact angles with liquids, for example with water; this results in a rapid distribution of the liquid over the surface and finally rapid running of the liquid film thus formed from the surface.

20 On the other hand, hydrophobic surfaces ensure drop formation owing to a large contact angle with liquids, such as water. High contact angles of up to 120°-130° are usually reached.

25 The use of hydrophobic materials, such as perfluorinated polymers, for the production of hydrophobic surfaces is known. A further development of these surfaces comprises structuring the surfaces in the μm to nm range. As a result of this, high contact angles of up to 150°-160° can be realized. Substantially more pronounced drop formation is observed and, in contrast to smooth surfaces, drops can 30 easily roll off slightly inclined surfaces.

U. S. Patent No. 5,599,489 discloses a process in which a surface can be rendered particularly water-repellent by bombardment with particles of an appropriate size and subsequent perfluorination.

Another process is described by H. Saito et al. in Surface Coating International 4, 1997, page 168 et seq. Here, particles of fluoropolymers are applied to metal surfaces. As a result, greatly reduced wettability of the resulting 5 surfaces by water and a considerably reduced tendency to icing are found.

U. S. Patent No. 3,354,022 and WO 96/04123 describe further processes for reducing the wettability of articles by topological changes of the surfaces. Here, artificial 10 protuberances and indentations having a height of about 5 to 1,000 μm and a spacing of about 5 to 500 μm are applied to hydrophobic materials or materials rendered hydrophobic after structuring. Surfaces of this type lead to rapid drop formation, where the drops rolling off pick up dirt particles 15 and thus clean the surface. Data on an aspect ratio of the protuberances are not available.

The processes presented above permit the production of surfaces which are completely and uninterruptedly liquid- and/or dirt-repellent. However, this is frequently not desired 20 and instead it is wished to produce surfaces which have liquid-repellent and liquid-wetting regions. Surfaces having such an "intelligent" structure are described, for example, in WO 94/27719. Here, a process for the production of generally 25 hydrophobic surfaces but having hydrophilic and functionalized regions is disclosed. These regions are hydrophilized by a radiochemical method and then functionalized by a wet chemical method. Surfaces of this type have up to 10,000 functionalized regions per cm^2 and are used in biological analysis, especially 30 in DNA sequencing. The amounts of the liquid which adhere to the functionalized regions are very small, being 50 μl to 2 μl , and can therefore be applied only by an automatic apparatus.

The chemical hydrophilization with subsequent 35 functionalization is often insufficient for distribution of liquids to define locations. Rather, it is desirable to have surfaces with a very large difference in the adhesion behavior

or in the contact angle of liquid-repellent and liquid-wetting regions.

5 This applies in particular when applied solutions are to be concentrated and the resulting concentrate or the dissolved substance is still to be present at a defined location.

10 It is therefore a major object of the present invention to develop articles having surfaces which have regions that are liquid-repellent and regions that are liquid-wetting in a defined location, the liquid-repellent regions having a very high contact angle with respect to liquids such as water or liquids having a low surface tension and thus promoting the running of these liquids into the liquid-wetting regions.

15 It was found that liquids on structured surfaces having protuberances of specific height and spacing and a surface energy of the material of the structured surface of less than 35 mN/m run rapidly and cleanly into regions of the surface which are of a defined location or collect there, 20 provided that these regions have liquid-wetting properties.

In the case of the surfaces according to the invention, the liquids run off even on gentle vibration or slight inclination of the surface or of the article by a few degrees.

25 The present invention therefore relates to articles having structured surfaces which have protuberances having a mean height of 50 nm to 10 μm and a mean spacing of 50 nm to 10 μm between one another, a surface energy of the unstructured material of less than 35 mN/m and liquid-wetting regions.

30 The present invention furthermore relates to processes for the production of the surfaces structured according to the invention. In one embodiment, surfaces having a surface energy of less than 35 mN/m can be provided mechanically or lithographically with protuberances and liquid-wetting regions without protuberances.

5 The regions without protuberances are flat surfaces without the protuberances of the structured surface. They may certainly have small structures, which however do not have the dimensions of the protuberances as defined in this specification. If the regions without protuberances are to possess small structures, they reach not more than 10% of the height of the protuberances of the structured surface. The regions without protuberances or "flat regions" can however be present on coarser superstructures, as will be shown.

10 In another process for the production of the surfaces according to the invention, surfaces having a surface energy of less than 35 mN/m can be provided mechanically or lithographically with protuberances, and regions of the structured surface thus obtained can then be coated to render it liquid-wetting.

15 As already mentioned, the protuberances can have a mean height of 50 nm to 10 μ m and a mean spacing of 50 nm to 10 μ m between one another. However, other heights and spacings are also possible; thus, independently of one another in each 20 case, the mean height and the mean spacing of the protuberances can be 50 nm to 10 μ m or 50 nm to 4 μ m. In addition, the protuberances may simultaneously have a mean height of 50 nm to 4 μ m and a mean spacing of 50 nm to 4 μ m. Particularly 25 preferably, the mean height is from about 0.5 to 10 μ m and the mean spacing is from about 0.5 to 10 μ m.

20 Surfaces structured according to the invention have particularly high contact angles, except for the liquid-wetting regions. This substantially prevents the wetting of the surface and leads to rapid drop formation. With an 30 appropriate inclination of the surface, the drops can roll off the protuberances and adhere to the liquid-wetting regions. The residue-free contraction of the drop front on concentration of a drop on the liquid-repellent surface is comparable with the behavior of a drop rolling off the liquid-repellent 35 surface. Here, the residues remain on the liquid-wetting regions.

Surfaces in the context of the present invention are hydrophobic in the liquid-repellent regions if the unstructured material has a surface energy of less than 35 mN/m, preferably 10-20 mN/m, and additionally oleophobic if the material has a 5 surface energy of less than 20 mN/m. This property extends the application of the structured surfaces also to areas where they come into contact with oil-containing liquids or other organic liquids or solutions having a low interfacial tension (e. g. as sample carriers used in the analysis of organic 10 compounds).

For adhesion to a surface or for multiplication on a surface, bacteria and other microorganisms require water, which is not available on the hydrophobic surfaces of the present invention. Surfaces structured according to the 15 invention prevent the growth of bacteria and other micro-organisms on the liquid-repellent regions; they are thus also bacteriophobic and/or antimicrobial. However, under appropriate boundary conditions, such as atmospheric humidity and temperature, the surfaces structured according to the 20 invention permit growth of bacteria and other microorganisms in a defined location on the wettable regions. Since the underlying effect is based not on antimicrobial active ingredients but on a physical effect, impairment of growth of the bacteria and other microorganisms on the liquid-wetting 25 regions by the liquid-repellent regions, for example by bleeding and/or diffusion of active ingredients, is ruled out.

The characterization of surfaces with respect to their wettability can be effected by measuring the surface energy. This quantity is obtainable, for example, by measuring 30 the contact angle of various liquids on smooth material (D. K. Owens, R. C. Wendt, J. Appl. Polym. Sci. 13, 1741 (1969)) and is stated in mN/m (milliNewton per meter). Determined by Owens et al., smooth polytetrafluoroethylene surfaces have a 35 surface energy of 19.1 mN/m, the contact angle (an advancing contact angle) with water being 120°. In general, hydrophobic

5 materials have contact angles (advancing contact angles) of over 90° with water. With a surface energy of 29-30 mN/m (depending on the molecular structure), polypropylene has, for example, an advancing contact angle of about 105° with respect to water.

10 The contact angle or the surface energy is expediently determined on smooth surfaces in order to ensure better comparability. The material properties of "hydrophobicity", "liquid repellent" or "liquid wetting" are also determined by the chemical composition of the uppermost molecular layers of the surface. A larger contact angle or lower surface energy of a material can therefore also be achieved by coating methods.

15 Surfaces according to the invention have larger contact angles in the liquid-repellent regions than the corresponding smooth surface or the liquid-wetting regions. The macroscopically observed contact angle is thus a surface property which reflects the material properties plus the surface structure.

20 The size and the shape of the liquid-wetting regions may vary widely. When the liquid-wetting regions are circular, for example, a preferred diameter may be from about 10 to 1,000 µm.

25 The liquid-wetting regions of the surfaces according to the invention have smaller contact angles than the liquid-repellent regions. This can be achieved by different surface structures, a different interfacial chemistry or a combination of the two on the respective regions:

30 - the liquid-wetting regions have the same protuberances but a higher surface energy than the remaining surface (i. e., liquid-repellent regions). The different surface energy can be achieved by a different interfacial chemistry (i. e., a different material), e. g. by coatings.

35 - the liquid-wetting regions have the same surface chemistry (i. e., same material) but different protuberances

compared with the remaining surface (i. e., liquid-repellent regions). The surface chemistry does not differ over the entire surface. Ideally, the liquid-wetting regions have no protuberances.

5 - the liquid-wetting and liquid-repellent regions have different protuberances and surface chemistry. This means that the material of the liquid-wetting regions has a higher surface energy than the remaining surface (i. e., the liquid-repellent regions), determined in each case as a smooth 10 surface.

A very wide range of processes can be used for the production of the surfaces according to the invention. Two variants are to be presented below.

Variant A)

15 The unstructured surfaces initially have a surface energy of less than 35 mN/m and are provided mechanically or lithographically with protuberances of the height and spacings of the liquid-repellent regions. Regions of the surface can then be coated to render them liquid-wetting. For this 20 purpose, for example, the structured surface can be covered with a mask which leaves the regions to be treated exposed. The unprotected regions can then be activated by physical methods. Plasma, high-frequency of microwave treatment, electromagnetic radiation, such as, for example, lasers or UV 25 radiation in the range 180-400 nm, electron beams or flame application, can be used here. By means of these methods, free radical areas which rapidly form hydroxyl, hydroperoxide or other polar and hence liquid-wetting functional groups in air or in an oxygen atmosphere are produced thermally or 30 photochemically on the material surface.

This physical method can be followed in the second step by a chemical modification which further improves the liquid-wetting properties. The functional groups are further reacted with stable terminal groups, such as, for example, 35 monomers capable of free radical polymerization. An example of such a chemical modification is the free radical graft

polymerization of vinyl monomers, such as, for example, acrylamide or acrylic acid, which takes place sufficiently rapidly as a result of the thermally initiated, free radical decomposition of the hydroperoxide groups above 70°C.

5 In practice, providing the regions with the liquid-wetting coating by means of electromagnetic radiation has proven useful.

Variant B)

10 In a further embodiment of the present invention, an unstructured surface can be provided mechanically or lithographically with protuberances. This surface is then coated with a material having a surface energy of less than 35 mN/m and the coating is removed again mechanically or lithographically from regions of the structured surface thus obtained.

15 Expediently, an unstructured material having a surface energy of more than 35 mN/m, preferably 35-75 mN/m, is used. After removal of the coating, the liquid-wetting regions have very substantially the properties of the original material.

20 Materials for producing bodies of articles having a surface energy of more than 35 mN/m are well known in the art. They include a variety of organic and inorganic materials, including typical engineering plastics such as acrylic resins, polyesters, polyamides, polycarbonates and the like.

25 Since in particular the chemical properties of the uppermost monolayers of the material are decisive for the contact angle, a surface modification with compounds which contain hydrophobic groups may be sufficient. Processes of this type include the covalent binding of monomers or oligomers to the surface by a chemical reaction, for example 30 treatments with fluoroalkylsilanes, such as Dynasilan* F 8261 (Sivento Chemie Rheinfelden GmbH, Rheinfelden) or with fluorinated ormocers.

35 Processes in which initially free radical areas which react, in the presence or absence of oxygen, with monomers capable of free radical polymerization are produced

*Trade-mark

on the surface may furthermore be mentioned. The activation of the surfaces can be effected by means of plasma, UV- or α -radiation or special photoinitiators. After the activation of the surface, i. e. production of free radicals, the 5 monomers can be polymerized on. Such a process generates a mechanically particularly resistant coating.

The coating of a material or of a surface, already structured according to the invention, by plasma polymerization of fluoroalkenes or vinyl compounds has proven particularly 10 useful. The vinyl compounds may also be partly fluorinated or perfluorinated.

The provision of a structured or unstructured surface with a liquid-repellent coating by means of material having a surface energy of less than 35 mN/m can be effected by 15 fluoroalkylsilanes or, for example, by plasma polymerization of fluoroalkenes or perfluorinated or partly fluorinated vinyl compounds. The use of an HF hollow-cathode plasma source with argon as carrier gas and C_4F_8 as monomer at a pressure of about 0.2 mbar is furthermore possible. Even surface energies 20 of less than 20 mN/m are achievable hereby.

In addition, both the structured and the unstructured surface can be coated with a thin layer of a hydrophobic polymer. This can be effected in the form of a coating or by polymerization of corresponding monomers on the surface of the 25 article. The polymeric coating used may comprise solutions or dispersions of polymers, such as, for example, polyvinylidene fluoride (PVDF) or reactive coatings.

Suitable monomers for providing a liquid-repellent coating by polymerization on the materials or their structured 30 surfaces are in particular fluoroalkylsilanes, such as Dynasilan^{*} F 8261 (Sivento Chemie Rheinfelden GmbH Rheinfelden).

The removal of hydrophobic or liquid-repellent coatings or of the protuberances from regions of the structured surface can in turn be effected mechanically, 35 thermally, photoablatively or lithographically. This is possible mechanically by micromachining, for example by

- drilling or cutting. The tools can be very accurately positioned, for example by a CNC apparatus. A lithographic or thermal method is, for example, exposure to a laser in a wavelength range in which the coating material absorbs energy.
- 5 For example, for polymethyl methacrylate (PMMA), this is the case at 193 nm, which is why an ArF excimer laser is particularly suitable here for the ablation of the coating.

A particularly low surface energy is necessary in particular when not only hydrophobic but also oleophobic behavior is required. This is the case in particular with oily liquids. These in fact lead to wetting in the case of nonoleophobic surfaces, which has a permanent adverse effect on the stated properties. With such applications, the surface energy of the unstructured material should be below 15 20 mN/m, preferably 5 to 20 mN/m.

As already mentioned, smooth polytetrafluoroethylene surfaces have a surface energy of 19.1 mN/m. With hexadecane as liquid having a low surface tension, the contact angle (advancing contact angle) is 49°. Surfaces which are 20 modified with fluoroalkylsilanes, such as for example, Dynasilan^{*} F (from Sivento Chemie, Rheinfelden), have surface energies of less than 10 mN/m. Here, advancing contact angles of up to 80° are measured with hexadecane. At a surface 25 energy of 29-30 mN/m, the contact angle of polypropylene with respect to hexadecane is estimated at less than 10° (difficult to determine experimentally).

The surface properties of the liquid-repellent regions of the surfaces according to the invention are dependent on the height, the shape and the spacing of the 30 protuberances.

The ratio of height to width of the protuberances, the aspect ratio, is likewise important. The protuberances preferably have an aspect ratio of from 1 to 10 and particularly preferably from 1.2 to 5, especially preferably 35 from 1.5 to 3.

In addition to the structural properties of the material, the chemical properties thereof are also important for achieving the small contact angle of the liquid-repellent regions. Here, the chemical composition of the uppermost 5 monolayer of the material is particularly decisive. The liquid-repellent regions of the surfaces according to the invention are therefore preferably produced from materials which are already hydrophobic before the structuring of their surface. These materials include in particular poly(tetra- 10 fluoroethylene), poly(trifluoroethylene), poly(vinylidene fluoride), poly(chlorotrifluoroethylene), poly(hexafluoropropylene), poly(perfluoropropylene oxide), poly(2,2,3,3-tetrafluorooxetane), poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole), poly(fluoroalkyl acrylate), poly(fluoro- 15 alkyl methacrylate), poly(vinyl perfluoroalkyl ether) or other polymers of perfluoroalkoxy compounds, poly(ethylene), poly(propylene), poly(isobutene), poly(isoprene), poly(4-methyl-1-pentene), poly(vinyl alkanoates) and poly(vinyl methyl ethers) as homo- or copolymers. These materials can also be 20 used as a component of a polymer blend. Mixtures of polymers with additives which, in the shaping process, are aligned so that hydrophobic groups predominate at the surface are furthermore possible. Suitable additives are fluorinated waxes, for example those available under the trade-mark Hostafloous from 25 Hoechst AG.

The structuring of the surface can also be carried out after the provision of a material with a hydrophobic coating. Likewise, the chemical modification of the surface can be carried out by providing a liquid-repellent coating 30 after the shaping.

The shaping or structuring of the surfaces can be effected by embossing/rolling or simultaneously during the macroscopic shaping of the article, such as, for example, casting, injection molding or other shaping methods. Corresponding negative molds of the desired structure are required 35 for this purpose.

Negative molds can be produced industrially, for example by means of the Liga technique (R. Wechsung in Mikroelektronik, 9 (1995), page 34 et seq.). Here, one or more masks are first produced by electron-beam lithography

5 according to the dimensions of the desired protuberances. These masks serve for exposure of a photoresist layer by deep X-ray lithography, with the result that a positive mold is obtained. The last mask exposure can also serve for introducing the flat, subsequently liquid-wetting regions.

10 The spaces in the photoresist are then filled by electrodeposition of a metal. The metal structure thus obtained represents a negative mold for the desired structure.

The exposure of a photoresist layer can also be effected by laser holography. If the photoresist is exposed

15 orthogonally to wave interference patterns, a so-called moth's eye structure is produced, with the result that a positive mold is obtained. A further mask exposure can in turn serve for introducing the flat, subsequently liquid-wetting regions. The spaces in the photoresist are then

20 filled by electrodeposition of a metal. The metal structure thus obtained represents a negative mold for the desired structure.

If no flat, subsequently liquid-wetting regions have as yet been introduced into the metallic negative mold

25 thus obtained, the negative mold can be mechanically worked. Here, the structure can be mechanically removed at desired points by micromachining.

In another embodiment of the present invention,

30 the protuberances are arranged on a somewhat coarser superstructure.

The protuberances have the above-mentioned dimensions and can be applied to a superstructure having a mean height of 10 nm to 1 mm, preferably 50 μ m to 1 mm and a mean spacing of 10 nm to 1 mm, preferably 50 μ m to 1 mm.

35 The protuberances and the superstructure can, simultaneously or in succession, be mechanically embossed or applied by lithographic methods or by shaping.

The protuberances and the superstructure can have a periodic (i. e., regular) arrangement. However, stochastic (or random) distributions of the dimensions of the superstructure and of the protuberances, simultaneously or 5 independently of one another, are also permissible. In the case of stochastic structures, the roughness is generally defined by means of roughness parameters. The arithmetic mean roughness R_a , the average peak-to-valley height R_z and the maximum peak-to-valley height R_{max} may be stated as 10 characteristics for the surfaces according to the invention. Surfaces according to the invention may have values of 0.2 to 40, preferably 1 to 10 μm for R_a , 0.1 to 40, preferably 0.5 to 10 μm for R_z and 0.1 to 40, preferably 0.5 to 10 μm for R_{max} .

15 In the case of surfaces having a superstructure as well as in the case of surfaces having only a microstructure, desirably the shaping or structuring of the surfaces is effected in one operation. Subsequent imparting of hydrophobic properties to an already produced "doubly" structured 20 surface or chemical modification of such surface is of course also possible.

Surfaces produced according to the invention are generally transparent since the microstructure has a size of less than 400 nm and are therefore suitable for all applications 25 in which high transmission or good optical properties are important. The production or coating of sample carriers in optical analysis may be mentioned in particular here.

Surfaces according to the invention are therefore outstandingly suitable for the manufacture of products in 30 which liquids have to be distributed over small regions, such as, for example, sample carriers. If a sample carrier has a surface according to the present invention, the sample can be distributed in a simple manner over the liquid-wetting regions by gentle vibration or slight inclination of the surface or of 35 a corresponding article by a few degrees or can be applied to an exact location by micrometering, for example by means of a

hand pipette or an automatic pipetting apparatus. Solutions can then be evaporated to dryness selectively on the liquid-wetting regions and hence concentrated.

5 Another possibility for applying liquids to surfaces according to the invention is the application by automatic pipetting apparatus to an exact location. The diameter of the drop applied can far exceed in size the diameter of the liquid-wetting region (by a factor of two to a hundred, preferably two to fifty). On concentration of the liquid
10 without boiling, the drop decreasing in size continues to remain strictly localized in the liquid-wetting region.

A preferred use of the surfaces according to the invention is therefore for sample carriers in instrument analysis.

15 The distribution is further accelerated if the liquid-wetting regions are not isolated from one another but are connected to one another by channels or grooves which are likewise liquid-wetting. Consequently, the structured surfaces according to the invention can be used for the
20 production of sample carriers with liquid-conducting systems (microfluidics).

Another use of the surfaces according to the invention is in nano- or microtiter sample carriers. The nanotiter sample carriers have liquid-wetting regions for holding amounts of liquid of less than 1 μ l, and the micro-titer sample carriers accordingly 1-100 μ l.

25 In addition, the structured surfaces according to the invention can be used as a structured reaction site for reagents and analytes for diagnostic systems (Lab on Chip).
30 The liquid-wetting surfaces serve here as reaction sites which are isolated from one another by liquid-repellent regions.

Further uses of the structured surfaces according to the invention are the production of sample carriers or
35 storage media for substance libraries in combinatorial chemistry or for nucleotide synthesis. The liquid-wetting

surfaces serve here as reaction sites which are isolated from one another by liquid-repellent regions. The site establishes the composition of the chemical reagents used. The sample plates can be stored under desired conditions and specific 5 reaction products can be subsequently recovered from separate sites after storage.

The following example is intended to describe the present invention in more detail without limiting its scope.

Example:

10 A microstructured surface of an injection molded polymethyl methacrylate (PMMA) sample having a microstructure of protuberances with a mean spacing of 5 μm , a mean height of 5 μm and an aspect ratio of 3 was rendered hydrophobic with a fluoroalkylsilane (e. g. Dynasilan* F 8261). The 15 sample is adjusted on a table adjustable in a controlled manner in the XY direction. A 1-70 μm thick layer of PMMA material was ablated by means of an ArF excimer laser (e. g. LPX 100i from Lambda Physik for producing an image of an aperture, provided with a Schwarzschild mirrored lens) from 20 circular areas (diameter 30-100 μm) with 10-100 pulses (10 Hz) and an energy density of 0.5 Jcm^{-2} at a wavelength of 193 nm. Both the structure and the low-energy surface chemistry were locally destroyed thereby. The site of the local destruction is defined by the positioning of the table. 25 Water drops of up to about 3-5 mm diameter adhere to the ablated regions.

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CLAIMS:

1. An article having a surface comprising:
 - (A) liquid-repellent regions in which the surface has a microstructure of protuberances having a mean height of 50 mm to 10 μm and a mean spacing therebetween of 50 mm to 10 μm and the surface is made of a material having a surface energy of less than 35 mN/m determined as a smooth unstructured surface; and
 - (B) liquid-wetting regions.
- 10 2. The article according to claim 1, wherein the liquid-wetting region have no protuberances of the mean height and the mean spacing defined in claim 1.
- 15 3. The article according to claim 2, wherein the surface in the liquid-wetting regions is made of a material having a surface energy higher than the liquid-repellent regions, determined in each case as a smooth unstructured surface.
- 20 4. The article according to claim 1, wherein the liquid-wetting regions have the same protuberances as the liquid-repellent regions and a surface energy higher than the liquid-repellent regions.
5. The article according to any one of claims 1 to 4, wherein the protuberances have a mean height of 50 mm to 4 μm .
6. The article according to any one of claims 1 to 5, wherein the protuberances have a mean spacing of 50 mm to 4 μm .
- 25 7. The article according to any one of claims 1 to 6, wherein the protuberances have an aspect ratio that is a ratio of height to width, of 1 to 10.

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8. The article according to any one of claims 1 to 7, wherein the surface of the liquid-repellent regions is made of a material having a surface energy of less than 20 mN/m.

9. The article according to claim 8, wherein the surface 5 of the liquid-repellent regions comprises an uppermost monolayer formed by covalently binding thereto a fluoroalkylsilane, the uppermost monolayer having a surface energy of less than 10 mN/m.

10. An article which comprises an article body made of an 10 organic or inorganic material having a surface energy of more than 35 mN/m and a surface comprising:

(A) water-and oil-repellent regions in which the surface has a microstructure of protuberances having a mean height of 0.5 to 10 μm , a mean spacing therebetween of 0.5 to 10 μm and 15 an aspect ratio of 1 to 5 and the surface has an uppermost monolayer made of a material having a surface energy of less than 10 mN/m, and

(B) water-wetting regions which are free from protuberances and in which the surface is made of the organic 20 or inorganic material of the article body.

11. The article according to claim 10, wherein the water-wetting regions are circular and have a diameter of 10 to 1,000 μm .

12. The article according to claim 10 or 11, wherein the 25 uppermost monolayer of the water- and oil-repellent regions is made of a fluoroalkylsilane covalently bonded to a surface of the article body.

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13. The article according to any one of claims 10 to 12, wherein the article body is made of polymethyl methacrylate (PMMA).

14. A structured surface which has
 - a) protuberances having a mean height of 50 nm to 10 μm and a mean spacing of 50 nm to 10 μm ,
 - b) a surface energy of the unstructured material of less than 35 mN/m and
 - c) liquid-wetting regions.
15. The structured surface as claimed in claim 14, wherein the liquid-wetting regions have no protuberances.
16. The structured surface as claimed in claim 15, wherein the liquid-wetting regions have a higher surface energy than the remaining surface, determined in each case on the unstructured material.
17. The structured surface as claimed in claim 14, wherein the liquid-wetting regions have the same protuberances as the remaining surface and a higher surface energy than the remaining surface.
18. The structured surface as claimed in any of claims 14 to 17, wherein the protuberances have a mean height of 50 nm to 4 μm .
19. The structured surface as claimed in any of claims 14 to 17, wherein the mean spacing of the protuberances is 50 nm to 4 μm .
20. The structured surface as claimed in any of claims 14 to 17, wherein the protuberances have a mean height of 50 nm to 4 μm and a mean spacing of 50 nm to 4 μm .
21. The structured surface as claimed in any of claims 14 to 20, wherein the protuberances have an aspect ratio of 1 to 10.
22. The structured surface as claimed in any of claims 14 to 21, wherein the protuberances are applied to a superstructure having a mean height of 10 μm to 1 mm and a mean spacing of 10 μm to 1 mm.

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23. The structured surface as claimed in any of claims 14 to 22, wherein the unstructured material contains poly(tetrafluoroethylene), poly(trifluoroethylene), poly(vilylidene fluoride), poly(chlorotrifluoroethylene),
5 poly(hexafluoropropylene), poly(perfluoropropylene oxide), poly(2,2,3,3-tetrafluorooxetane), poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole), poly(fluoroalkyl acrylate), poly(fluoroalkyl methacrylate), poly(vinyl perfluoroalkyl ether) or other polymers of
10 perfluoroalkoxy compounds, poly(ethylene), poly(propylene), poly(isobutene), poly(isoprene), poly(4-methyl-1-pentene), poly(vinyl alkanoates) or poly(vinyl methyl ethers) as homo- or copolymers.

24. A process for the production of structured surfaces
15 as claimed in any of claims 14 to 16 and 18 to 23, wherein surfaces having a surface energy of less than 35 mN/m are provided mechanically or lithographically with protuberances and liquid-wetting regions without protuberances.

25. The process for the production of structured surfaces
20 as claimed in any of claims 14 and 17 to 23, wherein surfaces having a surface energy of less than 35 mN/m are provided mechanically or lithographically with protuberances and regions of the surface are then coated to render it liquid-wetting.

26. The process as claimed in claim 25, wherein the
25 liquid-wetting coating of the regions is produced by electromagnetic radiation.

27. The process for the production of structured surfaces as claimed in any of claims 1 to 9, wherein surfaces are provided mechanically or lithographically with protuberances
30 and then coated with a material having a surface energy of less than 35 mN/m and the coating of regions of the coated,

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structured surface thus obtained is removed again mechanically, thermally, photoablatively or lithographically.

28. The process as claimed in claim 27, wherein the coating with a material having a surface energy of less than 35 mN/m is effected by plasma polymerization of fluoroalkenes or vinyl compounds.

29. The process as claimed in claim 27, wherein the coating with a material having a surface energy of less than 35 mN/m is effected using fluoroalkylsilanes or alkylsilanes.

10 30. The use of structured surfaces as claimed in any of claims 14 to 23 for the production of sample carriers for instrumental analysis.

31. The use of the structured surfaces as claimed in any of claims 14 to 23 for the production of sample carriers with 15 liquid-conducting systems (microfluidics).

32. The use of the structured surfaces as claimed in any of claims 14 to 23 as a structured reaction site for reagents and analytes for diagnostic systems (Lab on Chip).

33. The use of the structured surfaces as claimed in any 20 of claims 14 to 23 for the production of nanotiter or microtiter sample carriers.

34. The use of the structured surfaces as claimed in any of claims 14 to 23 for the production of sample carriers or storage media for substance libraries in combinatorial 25 chemistry.

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Abstract:

The present invention relates to structured surfaces having protuberances having a mean height of 50 nm to 10 μm and a mean spacing of 50 nm to 5 μm , a surface energy of the unstructured material of less than 35 mN/m and liquid-wetting regions and processes for the production of such surfaces.

Structured surfaces according to the invention can be used for the production of sample carriers for instrumental analysis, of sample carriers with liquid-conducting systems (microfluidics), as a structured reaction site for reagents and analytes for diagnostic systems (Lab on Chip) or for the production of nanotiter or microtiter sample carriers.